

# PATENT SPECIFICATION

815,247



Date of Application and filing Complete

Specification: July 17, 1956.

No. 22074/56.

Application made in United States of America on July 19, 1955.

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Index at acceptance:—Class 15(2), A1A(1A4: 1A5:2), A1C1B.

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## COMPLETE SPECIFICATION

### ERRATA

#### SPECIFICATION NO. 815,247

- Page 1, Title, for "Woob" read "Wood".
- Page 2, line 41, for "bene" read "been".
- Page 3, line 63, after "had" insert "a".
- Page 3, line 95, for "sulphate" read "sulphite".

THE PATENT OFFICE,  
20th November, 1959

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15 cellulose derivatives, or the production of regenerated cellulose articles, must satisfy stringent requirements. For example, the cellulose used in the manufacture of cellulose acetate and other organic acid esters of  
20 cellulose should have a brightness of at least 90, as measured by a brightness meter against a standard based on magnesium oxide in accordance with TAPPI method T 217, to obtain a product having a good colour and  
25 clarity. When wood pulp is used as the source of the cellulose, relatively drastic bleaching is required to achieve this brightness. Conventional bleaching agents such as chlorine and hypochlorites tend to degrade  
30 the cellulose molecule, and these agents cannot therefore be used to obtain a pulp having the required degree of brightness without excessive degradation occurring.

To overcome this difficulty it has been  
35 suggested that part of the bleaching treatment should be carried out with chlorine dioxide, which does not degrade the cellulose molecule appreciably. It is however not easy to obtain a product having the required brightness  
40 by treating the pulp with chlorine dioxide alone, and therefore combined bleaching techniques have been proposed, in which the chlorine dioxide bleach is followed by a mild bleach with hydrogen peroxide or a hypo-  
45 chlorite. The use of hydrogen peroxide is

[Price 3/6]

treating a slurry of the material with chlorine dioxide, and then adding to the slurry a supplementary agent consisting of a sulphite, bisulphite or thiosulphate or a substance capable of reacting with a compound already  
65 contained in the slurry to form a sulphite, bisulphite or thiosulphate.

If desired, a bleach with a hypochlorite may follow that with the chlorine dioxide, so long as the pulp is not given an intervening wash.  
70 By means of this new process it is easily possible to obtain a substantially undegraded cellulose of brightness at least 90 and often above 92, and which retains this brightness on heating or extended storage. The new  
75 process also has the merit of employing chemicals that are inexpensive and readily available.

The wood pulp may first be subjected to a known preliminary purification process. In  
80 general, this preliminary purification should give a partially purified pulp having a high  $\alpha$ -cellulose level and containing only small amounts of impurities such as lignin or pentosans. It should also give a pulp which  
85 has the maximum possible brightness consistent with avoiding excessive degradation of the cellulose molecule. A particularly desirable method of carrying out this preliminary purification is that described in our 90

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## COMPLETE SPECIFICATION

### Bleaching Wood Pulps

We, COLUMBIA CELLULOSE COMPANY, LIMITED, of Prince Rupert, British Columbia, Canada, a Company incorporated in accordance with the Laws of the Province of British Columbia, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the bleaching of wood pulps.

Chemical cellulose, i.e. cellulose that is to be employed as a raw material in processes such for instance as the manufacture of cellulose derivatives, or the production of regenerated cellulose articles, must satisfy stringent requirements. For example, the cellulose used in the manufacture of cellulose acetate and other organic acid esters of cellulose should have a brightness of at least 90, as measured by a brightness meter against a standard based on magnesium oxide in accordance with TAPPI method T 217, to obtain a product having a good colour and clarity. When wood pulp is used as the source of the cellulose, relatively drastic bleaching is required to achieve this brightness. Conventional bleaching agents such as chlorine and hypochlorites tend to degrade the cellulose molecule, and these agents cannot therefore be used to obtain a pulp having the required degree of brightness without excessive degradation occurring.

To overcome this difficulty it has been suggested that part of the bleaching treatment should be carried out with chlorine dioxide, which does not degrade the cellulose molecule appreciably. It is however not easy to obtain a product having the required brightness by treating the pulp with chlorine dioxide alone, and therefore combined bleaching techniques have been proposed, in which the chlorine dioxide bleach is followed by a mild bleach with hydrogen peroxide or a hypochlorite. The use of hydrogen peroxide is

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however expensive. On the other hand owing to the tendency of hypochlorites to degrade the cellulose molecule, only a limited increase in the brightness of the product can be achieved by the use of these agents, if the cellulose molecule is not to be excessively degraded.

It is an object of the present invention to provide a process by means of which there can be obtained from wood pulp cellulose of a high degree of brightness which has not suffered excessive degradation.

According to the present invention, a wood pulp for, example a sulphite wood pulp, is bleached by a process which comprises treating a slurry of the material with chlorine dioxide, and then adding to the slurry a supplementary agent consisting of a sulphite, bisulphite or thiosulphate or a substance capable of reacting with a compound already contained in the slurry to form a sulphite, bisulphite or thiosulphate.

If desired, a bleach with a hypochlorite may follow that with the chlorine dioxide, so long as the pulp is not given an intervening wash. By means of this new process it is easily possible to obtain a substantially undegraded cellulose of brightness at least 90 and often above 92, and which retains this brightness on heating or extended storage. The new process also has the merit of employing chemicals that are inexpensive and readily available.

The wood pulp may first be subjected to a known preliminary purification process. In general, this preliminary purification should give a partially purified pulp having a high  $\alpha$ -cellulose level and containing only small amounts of impurities such as lignin or pentosans. It should also give a pulp which has the maximum possible brightness consistent with avoiding excessive degradation of the cellulose molecule. A particularly desirable method of carrying out this preliminary purification is that described in our

Application No. 5485/56 (Serial No. 787,307) in which the pulp, after being first given a preliminary bleach with chlorine or a hypochlorite, is treated by a process in which a high temperature alkali boil is followed by a low temperature alkali extraction. By means of this process it is possible to obtain a wood pulp having an  $\alpha$ -cellulose content above 99% and a viscosity above 150 centipoises, measured in a 1% solution of ethylene diamine according to TAPPI method T 230. The high viscosity of the product obtained is an indication that the cellulose molecule has not been excessively degraded during this preliminary purification.

After the preliminary purification, the pulp, as an aqueous slurry of consistency for instance between 1 and 20%, is bleached with chlorine dioxide. The slurry may be acid, neutral, or alkaline, but it is desirable that it should have a pH below about 9 and preferably between 5 and 9, as at these pH levels there is less tendency for the chlorine dioxide to be inactivated by conversion into chlorates, or to be reduced by substances present in the slurry. The preferred pH's may be achieved by adding an alkaline substance, such as sodium hydroxide or sodium carbonate, to the slurry at the start of the chlorine dioxide treatment. It may also be desirable to add further quantities of an alkaline substance during the chlorine dioxide treatment to counteract the tendency for the pH to fall owing to the formation of acid substances. Variation in the pH of the slurry may also be avoided by buffering it to the desired pH by means of a suitable agent, such as sodium bicarbonate, which may be added as such or formed *in situ* by passing carbon dioxide into a slurry to which sodium hydroxide or sodium carbonate has been added. The chlorine dioxide may be added to the slurry as a gas or for example as an aqueous solution. The amount used may be between about 0.08 and 0.6% of the weight of the pulp. (All the parts and proportions in this specification are by weight). This stage of the bleach may be effected at a temperature between about 4° and 100°C. for between about 5 and 360 minutes.

The pulp may then if desired be bleached with a hypochlorite without any intermediate washing step. If such a bleach is given, the conditions are naturally so chosen that no excessive degradation of the cellulose molecule takes place. While such treatment will not in itself give a pulp having the highest possible brightness, the brightness will be further increased by the next stage in the process. The amount of hypochlorite used, calculated as sodium hypochlorite and based on the weight of the pulp, is between about 0.05 and 1.2%. The time of treatment at a temperature between about 4 and 75°C. and at a pH between about 7 and 10 may be

between 10 and 360 minutes.

After the chlorine dioxide bleach, or after the hypochlorite bleach, if one is given, there is added to the slurry the supplementary agent. This may for example be sodium sulphite, potassium sulphite, ammonium sulphite, sodium bisulphite, potassium bisulphite, ammonium bisulphite, potassium thiosulphate or ammonium thiosulphate, or a substance such as sulphur dioxide capable of reacting with a compound already contained in the slurry to form one of these compounds. The quantity of supplementary agent added to the slurry should be sufficient to react completely with all the oxidising substances, such as 80 chloride dioxide and hypochlorite, which it then contains, and is normally between 0.12 and 1 gram-molecule for each 100 grams of pulp. The slurry at this stage may be at a pH between about 1 and 10, and may be 85 maintained at a temperature between 4° and 75°C. for about 1 to 60 minutes. It is essential to the success of this process that the pulp is not washed between the treatment with chlorine dioxide and the addition of the supplementary agent. It is believed that the reaction of the supplementary agent with substances already present in the slurry produces a transitory highly active bleaching potential which rapidly produces a very white 95 pulp. Whether this be so or not, it is possible by the new process to obtain pulps having a better combination of brightness with high viscosity, than can normally be achieved simply by acidifying the slurry in 100 which the chlorine dioxide bleaching has been carried out, or adding to it a hypochlorite.

To obtain a product having the highest brightness the pulp is strongly acidified, i.e. is brought to a pH below 4, and especially 1-3, at least towards the end of the treatment with the supplementary agent. This acidification may be effected by adding to a slurry which initially has a higher pH sulphur dioxide or sulphurous acid, the quantity of sulphur dioxide required usually being between about 0.2 and 5% of the weight of the pulp. The bleach under these conditions of acidity may be continued for 1-60 minutes at 4°-75°C. When a sulphite is formed directly by the addition of sulphur dioxide to a slurry which already contains a suitable alkaline compound sufficient sulphur dioxide may usefully be added to bring the pH below 4 and preferably between 1 and 3. On the other hand the slurry may be acidified with a mineral acid, e.g. sulphuric acid, especially when more than enough of a sulphite, bisulphite or thiosulphate has been added to react with all the oxidising matter present. It is also possible to acidify the slurry by using both sulphur dioxide and a mineral acid, whereby the advantage of the sulphur dioxide treatment is obtained with the maximum economy in the use of reagents. The pulp is then washed and

dried in the usual manner. If desired, the slurry may be neutralised immediately before the pulp is separated and washed in order to lessen the corrosive effect on the washing equipment.

The following Examples are given to illustrate the invention further. All the proportions of the reagents added to the slurry are based on the dry weight of the pulp.

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#### EXAMPLE I

A partially purified sulphite pulp having an  $\alpha$ -cellulose content of 96.77% and a brightness of 75.4 was mixed with water to form a slurry having a consistency of 7% and an initial pH of 7. 0.3% of chlorine dioxide was added to the slurry, which was then maintained at a temperature of 45°C. for 135 minutes, at the end of which time the pH had dropped to about 3.8. Sufficient sodium sulphite to react with residual chlorine dioxide was then added, together with 5% of sodium bicarbonate, and the slurry was held at 45°C. for 5 minutes, the pH being 7.8. After this 2.5% of sulphur dioxide was added to the slurry in the form of a 2% aqueous solution, and the slurry was maintained at 25°C. for 5 minutes. Finally the pulp was washed and dried. The cellulose so obtained had a brightness of 92.3 and a viscosity of 143 centipoises.

#### EXAMPLE II

The same partially purified pulp as in Example I was mixed with water to form a slurry having a consistency of 7%. To it was added 0.3% of chlorine dioxide and 5% of sodium bicarbonate, and the slurry was maintained at 45°C. for 45 minutes. Sufficient sodium sulphite was added to the slurry to react with all the oxidising substances which it then contained. The slurry was then held for 5 minutes at 45°C., the pH being 8.1. 2.5% of sulphur dioxide in the form of a 2% aqueous solution was then added, and the slurry was maintained at 25°C. for 5 minutes. Finally the pulp was washed and dried. The cellulose so obtained had a brightness of 92.1 and a viscosity of 145 centipoises.

#### EXAMPLE III

A slurry having a consistency of 7% was prepared as in the previous Examples, and was subsequently adjusted to pH 9 with sodium hydroxide; 0.15% chlorine dioxide was then added, and the slurry was maintained at 45°C. for 45 minutes. The slurry was then re-adjusted to pH 9 with sodium hydroxide, and 0.1% of sodium hypochlorite was added, the slurry then being held at 45°C. for 90 minutes. Sufficient sulphur dioxide was added to the slurry to react with the alkali to form sodium sulphite and also to reduce the pH to 2, and the slurry was then maintained at 45°C. for 5 minutes. Finally, the pulp was washed and dried. The cellulose so obtained had brightness of 90.0 and a viscosity of 132 centipoises.

#### EXAMPLE IV

A slurry was prepared and treated with chlorine dioxide and hypochlorite as in Example III. Thereafter the pH of the slurry was adjusted to 6.8 with sulphuric acid; sufficient sodium thiosulphate was added to react with the residual oxidising substances, and the slurry was held at 45°C. for 5 minutes and then acidified to pH 3 with further sulphuric acid. Finally, the pulp was washed and dried. The cellulose so obtained had a brightness of 90.7 and a viscosity of 132 centipoises.

#### WHAT WE CLAIM IS:—

1. Process for bleaching a wood pulp, 80 which comprises treating a slurry of the wood pulp with chlorine dioxide, and then adding to the slurry a supplementary agent consisting of a sulphite, bisulphite or thiosulphate or a substance capable of reacting with a compound already contained in the slurry to form a sulphite, bisulphite or thiosulphate.

2. Process for bleaching sulphite wood pulp, which comprises treating a slurry of the sulphite wood pulp with chlorine dioxide, and then adding to the slurry a supplementary agent consisting of a sulphite, bisulphite or thiosulphate or a substance capable of reacting with a compound already contained in the slurry to form a sulphate, bisulphite or thiosulphate.

3. Process according to Claim 1 or 2, wherein there is added to the slurry a sulphite, bisulphite or thiosulphate of sodium, potassium or ammonium, or sulphur dioxide. 100

4. Process according to any of the preceding claims, wherein the pH of the slurry after the addition of the supplementary agent is between 1 and 10.

5. Process according to any of Claims 1-3, wherein after the addition of the supplementary agent the pH of the slurry is between 4 and 10, and before the end of the treatment the pH is reduced below 4.

6. Process according to Claim 5, wherein the pH of the slurry is reduced by adding sulphuric acid to the slurry. 110

7. Process according to any of Claims 1-3, wherein there is added to the slurry sufficient sulphur dioxide to react with the alkali present to form a sulphite and also to reduce the pH of the slurry below 4.

8. Process according to any of Claims 5-7, wherein the pH is reduced to 1-3.

9. Process according to any of the preceding claims, wherein 0.12-1 gram molecule of the supplementary agent is added to the slurry for each 100 grams of the cellulosic material. 120

10. Process according to any of the preceding claims, wherein the slurry is treated with between 0.08% and 0.6% of chlorine dioxide, based on the weight of the cellulosic material. 125

11. Process according to any of the pre- 130

ceding claims, wherein the slurry is at a pH between 5 and 9 during the chlorine dioxide treatment.

12. Process according to any of the preceding claims, wherein the slurry is treated with the chlorine dioxide at a temperature between 4° and 100°C. for between 5 and 360 minutes.

13. Process according to any of the preceding claims, wherein between the chlorine dioxide treatment and the addition of the supplementary agent the slurry is given a treatment with 0.05-1.2% of a hypochlorite calculated as sodium hypochlorite and based

on the weight of the cellulosic material.

14. Process according to Claim 13, wherein the hypochlorite treatment is carried out at a pH between 7 and 10 and at a temperature between 4° and 75°C. for between 10 and 360 minutes.

15. Process for the bleaching of wood pulps substantially as described.

16. Bleached wood pulps obtained by the process of any of the preceding claims.

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